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Title: Los Alamos National Laboratory Methods for NWAL Measurements by MC-ICP-MS

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Los Alamos National Laboratory Methods for NWAL Measurements by MC-ICP-MS

IAEA Exchange

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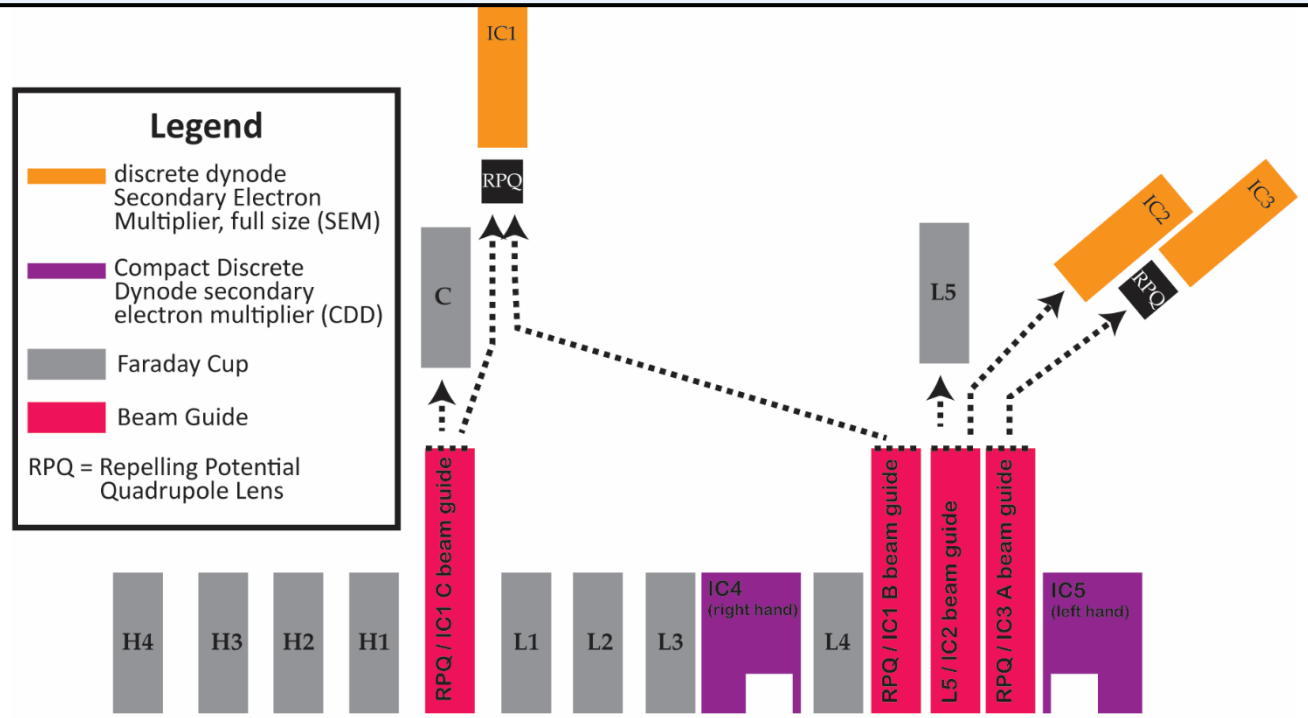
Analysis of NWAL Swipes

- Thermo Scientific Neptune Plus used to analyze swipe sample fractions
  - Multi-collector ICP-MS with desolvating sample introduction system
- Distinct cup configurations for measuring UxT (traced U) UxI (untraced U), and PuT/PuI (traced and untraced Pu) fractions
- Strategies for correcting instrumental effects
  - Mass bias, gain, abundance sensitivity



Traced U: Instrument Setup

UxT Sequence

- U Standard 1
- Washes 1-4
- U Standard 2
- Washes 1-4
- UxT Sample 1
- Washes 1-4
- UxT Sample 2
- Washes 1-4
- U Standard 1
- Washes 1-4
- U Standard 2
- ⋮

U Standard 1
(e.g. IRMM 74-1, U500)
Mass Bias Corrections

U Standard 2
(e.g IRMM 74-2)
$^{233}U/^{238}U$ similar to samples

Traced Uranium Neptune Plus Cup Configuration						
	L2	**L1**	**C**	**H1**	**H2**	
U Samples/QCs	233U	234U	235U	236U	238U	Ion Counter
U Standards	233U	234U	235U	236U	238U	Faraday

- UxT samples typically traced with 1:1 ratio of ^{233}U:^{238}U
- All U isotopes measured on Faradays
- Typically include standards with ^{233}U as bracketing standard and/or QC (**Standard 2)**
- Exponential mass bias corrections applied using $^{233}U/^{238}U$ or $^{233}U/^{235}U$ ratio of Standard 1

Untraced U: Instrument Setup

UxI Sequence

- U Standard 1
- Washes 1-4
- U Standard 2
- Washes 1-4
- U Standard 3
- Washes 1-4
- UxI Sample 1
- Washes 1-4
- UxI Sample 2
- Washes 1-4
- U Standard 1
- Washes 1-4
- U Standard 2
- Washes 1-4
- U Standard 3
- ⋮

Untraced U Samples
^{235}U on Faraday or IC

U Standard 1
(e.g. U010, U050, U500, U850)
Mass Bias and Gain Corrections

U Standard 2
(e.g. U005-A, U960, U010)
U composition similar to samples

U Standard 3
Gain Correction for ^{235}U on IC

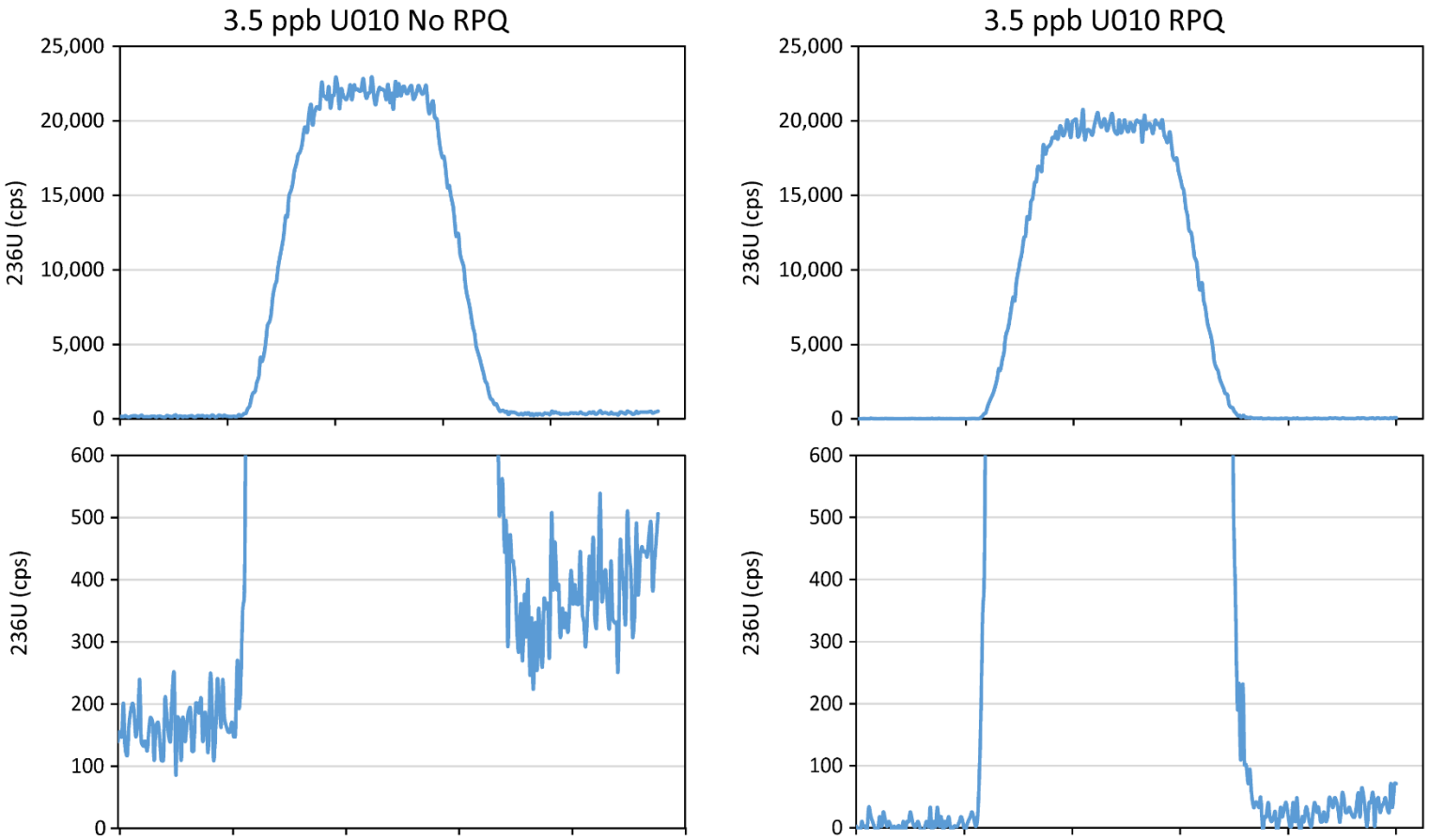
Untraced U Neptune Plus Cup Configuration						
	IC5	**IC3**	**IC2**	**L5**	**IC1 B**	**L4**
U Samples/Standards 2 & 3	233U	234U	235U	235U	236U	238U
U Standard 1	233U	234U	235U		236U	238U

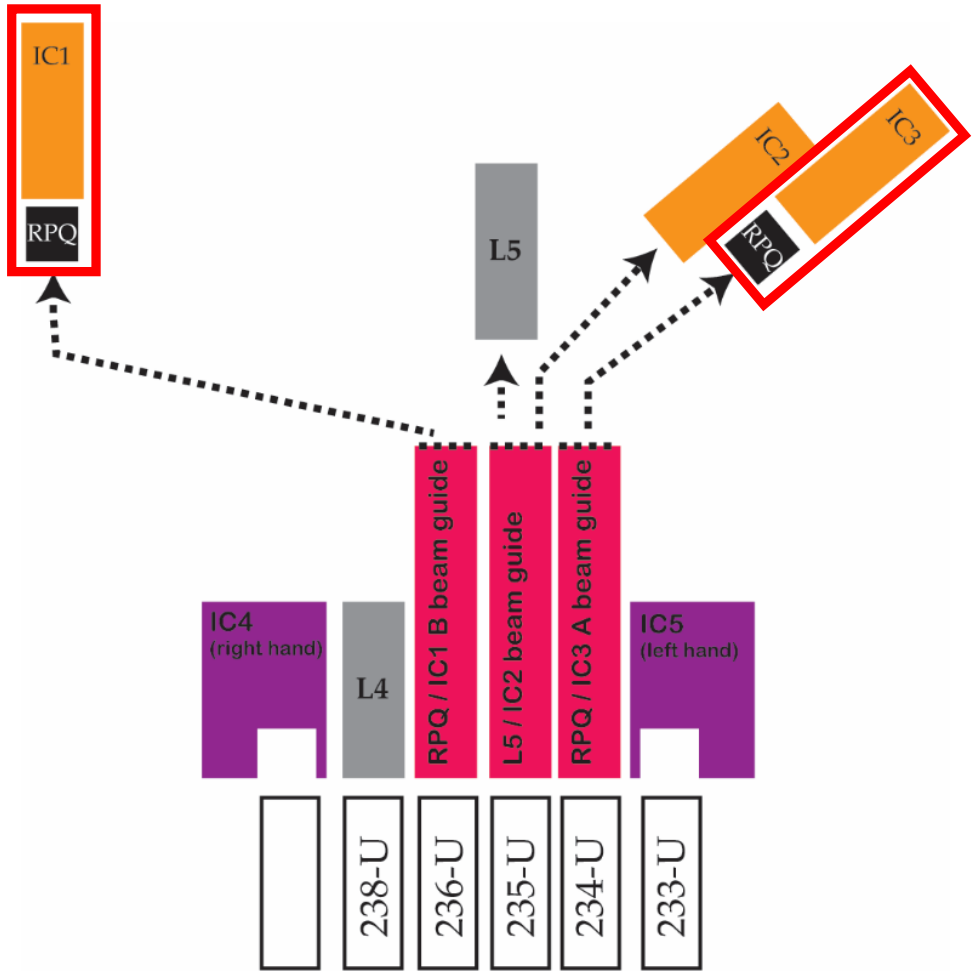
Ion Counter
Faraday

- U samples screened prior to analysis
  - Standards with similar U isotopic compositions selected as QCs (**Standard 2**)
- Separate Mass Bias and Gain Corrections
  - Exponential MB corrections using $^{235}U/^{238}U$ ratio (faraday-faraday; Standard 1)
  - Gain corrections for ion counter measurements using minor isotope ratios (Standard 1) and additional bracketing standard (Standard 3)

Untraced U: Abundance Sensitivity

- Tailing on ^{236}U or ^{234}U managed by RPQs (energy filters)
- RPQs reduce but do not always completely eliminate tailing on minor isotopes. And no RPQ available on IC5
  - Tailing also corrected by 4 point baseline method (when needed)





Untraced U: Abundance Sensitivity

- Baselines measured prior to each U standard and sample in the run
  - Capture any changes in tail magnitude that may result from plasma fluctuations throughout run
- Four baseline points measured to calculate exponential curve
  - 0.5 AMU above and below center mass
  - 0.35 AMU above and below center mass

Cup Configuration: pa_ic.ccf — Number of Blocks: 1 — Cycles/Block: 7 — Measure first line every: 1 cycles

Line No.	Mass Set	IC5	RPQ/IC3 A	IC2 L5	IC2 L5	RPQ/IC1 B	L4	L3	RPQ/IC1 C	Integration Time[s]	Number of Integrations	Idle Time [s]	Control Cup Peakcenter	Control Cup Focus	Jump Mode
1	05amu_Down	233U	234U	235U	235U	236U	238U		254.01	0.131	5	1.000	NONE	NONE	
2	035amu_Down	233U	234U	235U	235U	236U	238U		254.16	0.131	5	1.000	NONE	NONE	Normal
3	035amu_Up	233U	234U	235U	235U	236U	238U		254.86	0.131	5	1.000	NONE	NONE	Normal
4	05amu_Up	233U	234U	235U	235U	236U	238U		255.01	0.131	5	1.000	NONE	NONE	Normal

U Baseline Method
Run prior to each U standard/sample

Cup Configuration: pa_ic.ccf — Number of Blocks: 1 — Cycles/Block: 40

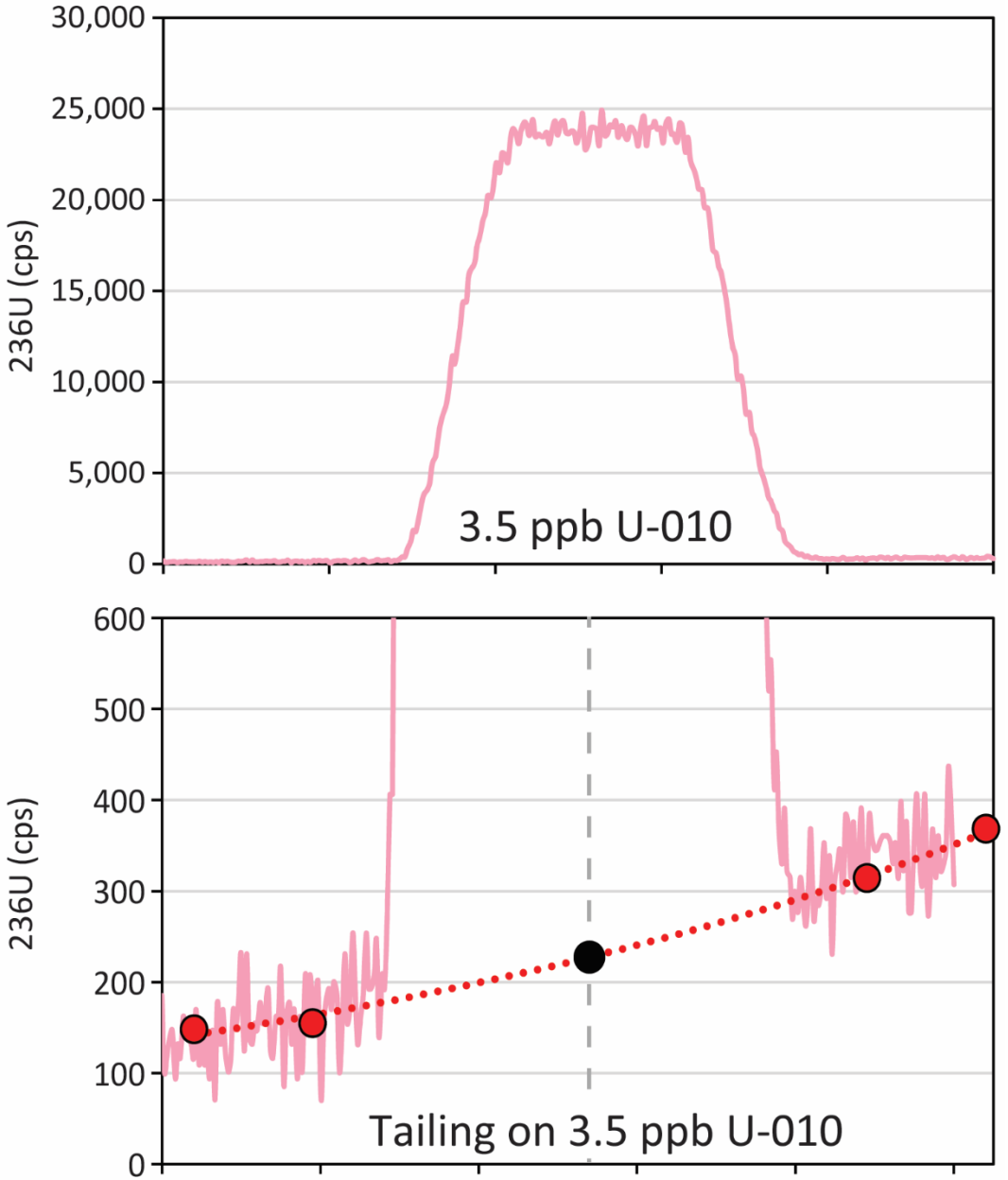
Line No.	Mass Set	IC5	RPQ/IC3 A	IC2 L5	IC2 L5	RPQ/IC1 B	L4	L3	RPQ/IC1 C	Integration Time[s]	Number of Integrations	Idle Time [s]	Control Cup Peakcenter	Control Cup Focus	Jump Mode
1	Main	233U	234U	235U	235U	236U	238U	242.692	254.51	4.194	1	3.000	NONE	NONE	

U Method

Untraced U: Abundance Sensitivity

U010 ^{236}U Baseline Measurements and Tail Calculations					
Cycle	0.50 amu below CM (cps)	0.35 amu below CM (cps)	0.35 amu above CM (cps)	0.50 amu above CM (cps)	Calculated 236 Tail at CM (cps)
1	146.49	144.97	279.25	354.02	214.05
2	143.44	155.65	305.19	375.38	224.89
3	138.86	144.97	294.51	364.70	215.64
4	157.17	155.65	321.97	367.75	231.99
5	163.28	163.28	326.55	367.75	237.87
6	166.33	172.43	352.49	367.75	246.93
7	123.61	149.55	323.50	384.53	218.98
Average:					**227.19**
STDEV:					**12.28**

Counts at four off-peak masses input into Excel growth function to calculate and subtract tailing



Pu Fractions: Instrument Setup

Pu Sequence

- Pu Standard 1
- Washes 1-5
- Pu Standard 2
- Washes 1-5
- Pu Sample 1
- Washes 1-5
- Pu Sample 2
- Washes 1-5
- Pu Standard 3
- Washes 1-5
- Pu Standard 1
- Washes 1-5
- Pu Standard 2
- ⋮

Traced/Untraced Pu Neptune Plus Cup Configuration				
	IC5	**IC3**	**IC2**	**IC1**
Pu Samples/QCs	239Pu	240Pu	241Pu	242Pu
Pu Standards	239Pu	240Pu	241Pu	242Pu

Ion Counter

Faraday

Pu Samples
All Pu isotopes on ICs

Pu Standard 3
(e.g. CRM 137; IRMM 081a)
Pu similar to samples

Pu Standard 1
(e.g. NBS-948/CRM 138)
Corrects $^{240}Pu/^{239}Pu$ and $^{241}Pu/^{239}Pu$ ratios

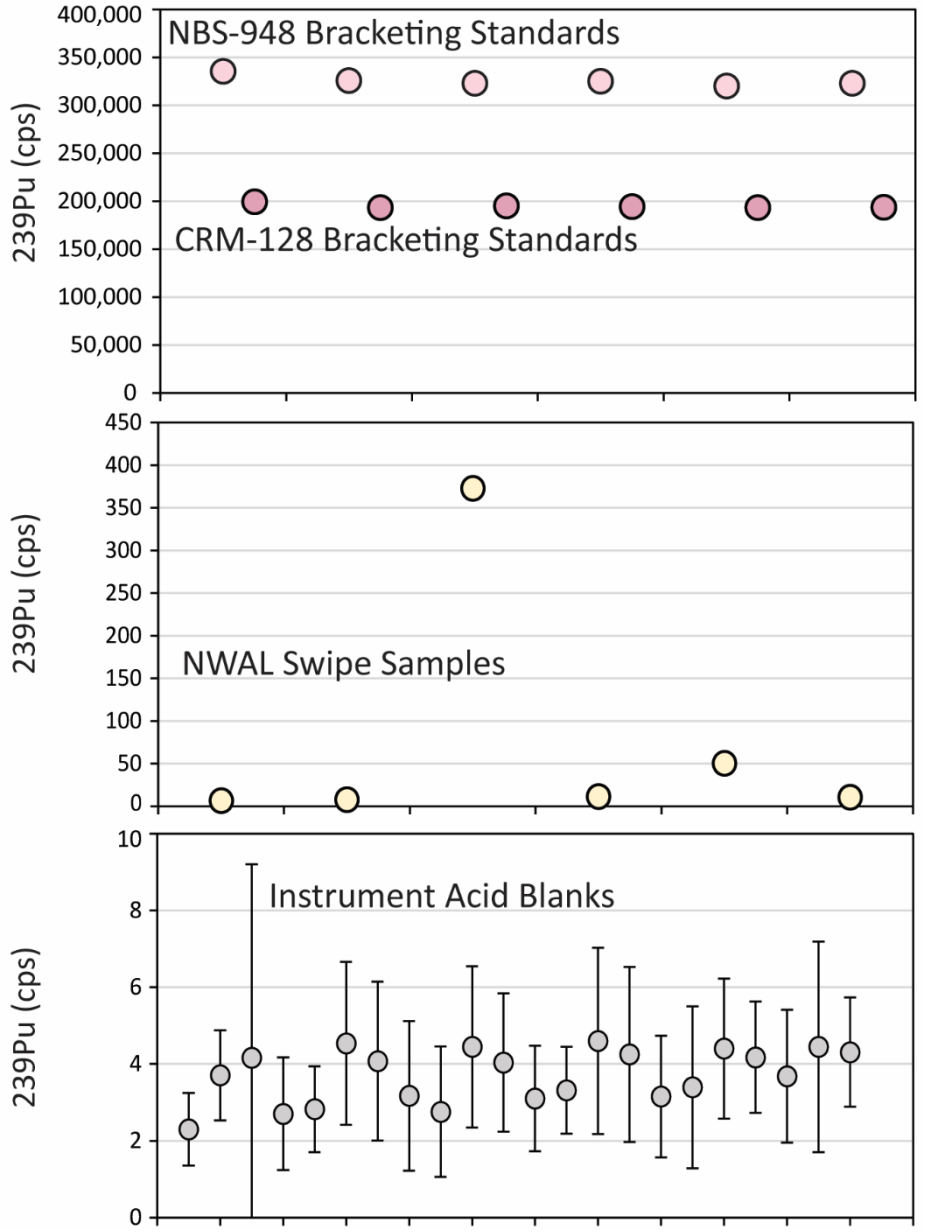
Pu Standard 2
(e.g. CRM 128)
Corrects $^{242}Pu/^{239}Pu$ ratios

- Traced Pu fractions spiked with ~6.5 pg ^{242}Pu
- Pu samples screened prior to analysis
  - Screen for Pu composition, as well as potential interferences (e.g. ^{238}U, ^{208}Pb, and ^{184}W)
  - Standards with similar Pu compositions selected as QCs (**Standard 3**)
- Combined Mass Bias and Gain Corrections
  - Use IC-IC measurements of Standard 1 **and** Standard 2

Pu Measurement Challenges

- Combined mass bias and gain corrections using IC-IC ratios of Pu standards **effective but not ideal**
  - Need to run bracketing standards at high enough concentrations to achieve reasonable precision.
  - Samples often have very low Pu contents (< 1 pg) so must also maintain low instrument backgrounds
  - Long washes required to achieve reasonable instrument limits of detection

Isotope Compositions of Pu Bracketing Standards			
	$^{240}Pu/^{239}Pu$	$^{241}Pu/^{239}Pu$	$^{242}Pu/^{239}Pu$
NBS 948	0.08611	0.000541*	
CRM 128			1.00063



The Future of Pu Measurements by ICP-MS?

Traced/Untraced Pu Neptune Plus Cup Configuration						
	IC5	**IC3**	**IC2**	**L5**	**IC1B**	**L4**
Pu Samples/QCs	239Pu	240Pu	241Pu		242Pu	
U Standard/QC	233U	234U	235U	235U	236U	238U
	236U		238U			

Ion Counter

Faraday

Move towards using U as bracketing standard for Pu samples

- **Advantages**
  - Achieve lower Pu instrument blanks with fewer washes
  - Better sample precision: $^{235}U/^{238}U$ (Faraday-Faraday) ratio for mass bias and potentially better counting statistics on minor isotope (IC-Faraday) ratios for gain corrections
- **Concerns**
  - Abundance sensitivity issues in bracketing U standards (RPQs vs. Baselines?)
  - No RPQ on IC5. Baselines with careful standard selection to minimize ^{238}U tail on ^{236}U?

NWAL Sample Analysis by MC-ICP-MS: Summary

- **UxT measurements**: Faraday measurements
  - Mass bias corrections with $^{233}U/^{238}U$ or $^{233}U/^{235}U$ (Faraday-Faraday) ratios
- **UxI measurements**: combination of ion counters and Faradays
  - Mass bias corrections made with $^{235}U/^{238}U$ ratios (Faraday-Faraday)
  - Gain corrections made using minor U isotope ratios (ion counter-Faraday)
  - Abundance sensitivity improved using RPQs and baseline measurements
- **PuT Measurements**: Ion counter measurements
  - Combined mass bias and gain corrections using Pu standards
  - Move towards U standards to correct for instrumental effects and to improve precision?